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Preparation of hydrophobic poly(isobutylene) star polymers with hydrophilic poly(propylene imine) dendritic cores

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Summary

Poly(propylene imine) dendrimers with amino chain ends have been used for the preparation of hydrophobic star polymers with hydrophilic dendritic cores. The unsaturated end groups of polyisobutylene (PIB) were transformed into reactive anhydride end groups by an "ene" reaction with maleic anhydride, and the resulting functionalized PIB was then reacted with dendrimers to afford dendrimer-PIB star copolymers.

Introduction

Dendrimers are highly branched macromolecules that emanate from a central core. In the last ten years, interest in this area has been growing rapidly due to the unique structure and properties of dendrimers (1). The preparation of dendritic macromolecules by the divergent (2) and convergent (3) growth approaches has been well documented, and a large number of dendrimers have been prepared. Meanwhile applications for this novel type of macromolecules are being explored (1).

Poly(propylene imine) dendrimers (4) constitute one of the two currently commercially available families of dendrimers. Distinguished from most other dendrimers, these dendrimers are hydrophilic due to their tertiary amine structure in the interior and primary amine structure in the periphery. As a result, they are miscible with water in all proportions. The number of amino end groups varies from 4 (for G-1) to 64 (for G-5) depending on the generation.

The primary amino groups at the chain ends are very reactive and several modification reactions have been reported. Among these, perhaps the most remarkable work was the "dendritic box" (5a), in which guest molecules, such as Rose Bengal, were encapsulated in the internal cavities of the dendrimer when a protected amino acid was attached to each end group at the periphery of the dendrimer. The selective liberation of encapsulated guests could then be achieved by a chemical deprotection step based on the shape and size of the guest molecules (5b). These dendrimers have also been modified with short alkyl chains to produce inverted unimolecular micelles (6), with chiral compounds to afford chiral catalysts (7), with poly(phenylene ether) to make star-shape polymers (8), with cyanobiphenyl mesogens to afford liquid crystalline dendrimers (9) and with saccharides to make glycodendrimers (10).

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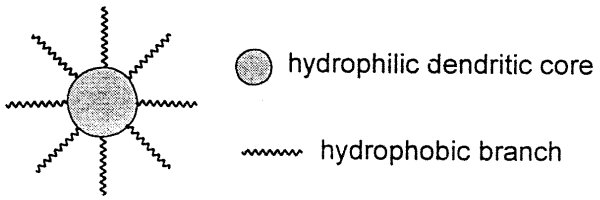
Figure 1. Graphical representation of hydrophobic star polymers with hydrophilic dendritic core



Here we present our work towards the preparation of star-shaped polymeric materials with unique structure/composition based on poly(propylene imine) dendrimers. As shown in Figure 1, this type of material consists of a hydrophilic dendritic core surrounded by hydrophobic branches. The core size and the number of arms are controllable by varying the generations of dendrimers used, while the arm length can be adjusted by attachment of different hydrophobic chains. Therefore, these star polymers possess well-defined structure with controllable core size and arm length. End reactive polyisobutylene (PIB) was selected for the hydrophobic branches. Other PIB-based star polymers have been reported previously (11). For example, Kennedy et al have prepared an 8-arm star PIB by polymerization of isobutylene with an octa-functional initiator (11a), while Faust et al have reported an amphiphilic A_2B_2-type star block copolymer (A = PIB and B = poly(methyl vinyl ether)) by a living coupling reaction (11b). Our strategy is to use poly(propylene imine) dendrimers as multifunctional cores and attach end reactive PIB to the cores by a simple coupling reaction. The resulting star-like amphiphilic copolymers are expected to be useful as prototypes for high performance lube oil additives, specialty adhesives, lubricants, and viscosity reducing agents.

Experimental

Materials

Poly(propylene imine) dendrimers (G-1 to G-5) were purchased from DSM. Two polyisobutylene samples with olefinic end groups (PIB-U), Mn 1,000 (denoted as PIB1) and 2,300 (denoted as PIB2), were obtained from Exxon Chemical Company. All other chemicals were purchased from Aldrich and used without further purification.

Characterization

^{1}H-NMR spectra were recorded on a Bruker AMX-300 (300 MHz) spectrometer in $CDCl_3$ with the solvent proton signal as the internal standard. Infrared samples were prepared as a thin film (neat) on a silicon wafer and measured on a Nicolet IR/44 spectrophotometer. The content of anhydride groups in functionalized PIB was determined by titration with sodium methoxide using thymol blue as an indicator. HPLC analysis was performed on a 15 cm x 4.6 mm. i.d. column (for analytical HPLC) or a 30 cm x 8 mm i.d. column (for preparative HPLC) packed with porous monodisperse poly(2,3-dihydroxypropyl methacrylate-co-ethylene dimethacrylate) beads (14), and a gradient of acetone in hexane was used as a mobile phase. The analytical HPLC system consisted of three Waters 510 pumps, a Waters 717 plus autosampler and an evaporative light-scattering detector PL-ELSD 960 from Polymer Laboratories. In the case of preparative separation the autosampler was replaced by a Rheodyne 7725i manual injector equipped with a 12 mL loop and the fractions of effluent were collected through a switching valve (modified Pheodyne injection valve) that was used for occasional 1 second long switches from fraction collector to ELSD for polymer detection.

General Procedure for the preparation of PIB with anhydride end groups (PIB-SA) This reaction was performed according to a literature procedure (12). PIB and maleic anhydride (6 equiv. per "exo" double bond) were mixed and heated at 190 °C under N_2 (9 hrs for PIB1 and 18 hrs for PIB2). After cooling to room temperature, the reaction mixture was dissolved in hexane and filtered. The filtrate was concentrated to a small volume then precipitated into a large volume of acetone. The supernatant solution was decanted, and the viscous liquid was collected and dried at 110 °C under vacuum overnight, yielding the desired product as a viscous yellow liquid.

General Procedure for the preparation of Dendrimer-PIB copolymers Dendrimer and PIB-SA (1.1 equiv. of anhydride per amino end group) were mixed in toluene and heated at 100 °C under N_2 overnight. Toluene was distilled off, and the liquid residue was dried under vacuum at 100 °C overnight to afford the crude product as a viscous yellow liquid.

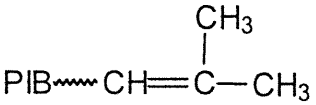
General Procedure for the Purification of Dendrimer-PIB1 copolymers To a stirred solution of the crude product in hexane, an equal volume of acetone was added dropwise. After the addition was complete, the solution was stirred for 30 min. The white cloudy supernatant solution was decanted, and the viscous yellow liquid was collected. The same procedure was repeated 5 times. The product was dried under vacuum at 100 °C.

General Procedure for the Purification of Dendrimer-PIB2 copolymers The product was purified for analytical purposes by preparative HPLC as describe above.

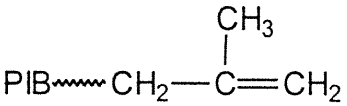
Results and Discussion

1. Functionalization of polyisobutylene with olefinic end groups (PIB-U).

The starting PIB used in this study contains two types of olefinic chain ends ("exo" and "endo"); their structures are shown below.



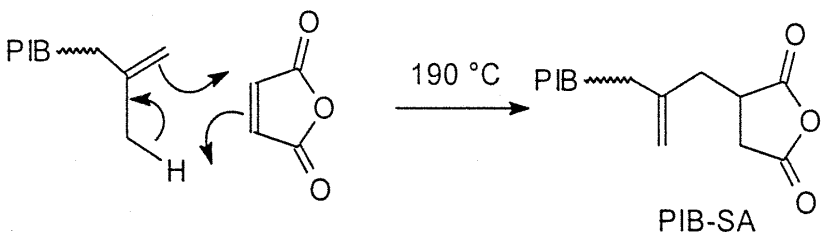
"endo"



"exo"

Because the double bonds of PIB cannot react directly with the amino groups of the poly(propylene imine) dendrimers, a functionalization reaction with maleic anhydride was carried out to convert the olefins to anhydride end groups. This reaction was selected because it is an easy, clean, and well-documented functionalization; in addition, the resulting anhydride is highly reactive toward the amino groups of dendrimers. This type of reaction, studied in detail by Tessier et al (13) and Walch et al (12), proceeds through the "ene" reaction mechanism (Scheme 1) in which only "exo" double bonds can react.

Scheme 1.



PIB-SA

The conversion of the "exo" double bonds to anhydride can readily be monitored by FTIR. The starting polymer with olefinic chain ends has an absorption at 1645 cm^{-1}, and does not absorb in the 1700-2000 cm^{-1} region (Figure 2a). After reaction (Figure 2b), the double bond absorption has disappeared, while two bands corresponding to the carbonyl groups of the anhydride moieties appear at 1867 and 1790 cm^{-1}. The small peak at 1700 cm^{-1} is due to the hydrolysis of a few anhydride groups. ^{1}H-NMR also supports the transformation of double bonds to anhydride. The spectrum of the starting PIB (Figure 3a) includes two main peaks at 4.64 and 4.85 ppm corresponding to the protons of the "exo" double bonds, and a minor peak at 5.15 ppm corresponding to the "endo" double bonds. As seen in Figure 3b, after reaction with maleic anhydride, the two main peaks disappear almost completely while a new peak due to the protons from newly formed double bond appears at 4.90 ppm. The peak at 5.15 ppm remains unchanged because the "endo" double bonds cannot react with maleic anhydride. Close examination of the NMR spectrum reveals the existence of a peak at 5.28 ppm that may be assigned to the olefinic protons from another "ene" reaction involving extraction of the protons from allylic methylene groups rather than from allylic methyl groups (13). Several small peaks seen around 5.15 ppm are due to the hydrolysis of anhydride groups. The PIB-SA obtained by this method consists of three major components, the desired functionalized PIB-SA, unreacted PIB with "exo" double bonds and unchanged PIB with "endo" double bonds. The content of anhydride end groups was determined by titration with sodium methoxide as 0.507 mmol/g polymer for PIB1-SA and 0.227 mmol/g polymer for PIB2-SA. The degree of functionalization was calculated as 0.51 for PIB1-SA and 0.52 for PIB2-SA based on Mn 1,000 and 2,300, respectively. The degree of functionalization is relatively low due mainly to the fact that at least 15% of starting PIB has "endo" double bonds that are unreactive in the functionalization reaction. Another reason is inherent to a flaw in the calculation since it is based on the molecular weight of the starting PIBs. In fact, the molecular weight of the polymer increases because of the loss of low molecular weight species during precipitation.

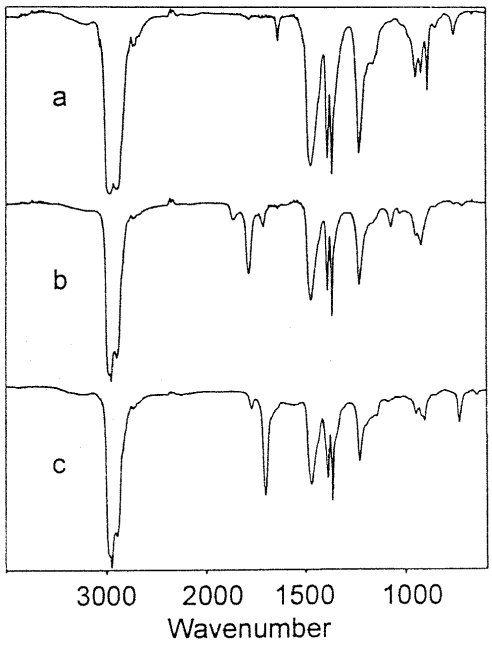


Fig 2. IR spectra: (a) PIB1, (b) PIB1-SA and (c) G-3 dendrimer-PIB1 copolymer.

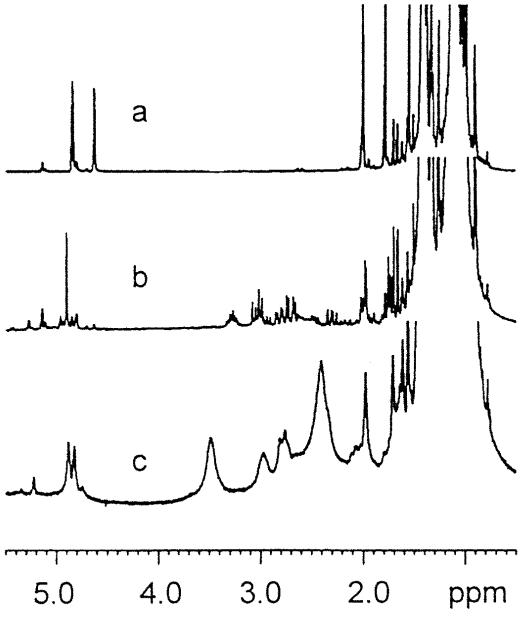


Fig 3. ^{1}H-NMR spectra: (a) PIB1,(b) PIB1-SA and (c) G-3 dendrimer-PIB1 copolymer.

2. Preparation of dendrimer-PIB copolymers

The anhydride groups react easily with the amino groups of the dendrimers to form amic acid functionalities that may be converted to stable imide bonds. The reaction was performed by refluxing a solution of PIB-SA and dendrimer in toluene. Scheme 2 shows the reaction between a G-3 dendrimer and PIB-SA. The anhydride ring is opened by the amine to afford an amide and a carboxylic acid, and the ring is then closed again with loss of a water molecule. Figure 2c shows the FTIR spectrum of the product from G-3 dendrimer and PIB1-SA, the peaks (1867 and 1780 cm^{-1}) characteristic of the anhydride of PIB-SA shift to lower wavenumber (1772 and 1705 cm^{-1}) after reaction, suggesting the formation of the imide bonds while no remaining anhydride band can be observed. The copolymers were also characterized by ^{1}H-NMR. Figure 3c shows the proton spectrum of the G-3 dendrimer-PIB1 copolymer. Although the large peaks for the protons of the PIB chains make the detection of other protons difficult, several small peaks can still be seen at 2.0-6.0 ppm. These correspond to the protons from the dendritic core and from the linkage between the dendritic core and the PIB chains, supporting the formation of the dendrimer-PIB copolymers.

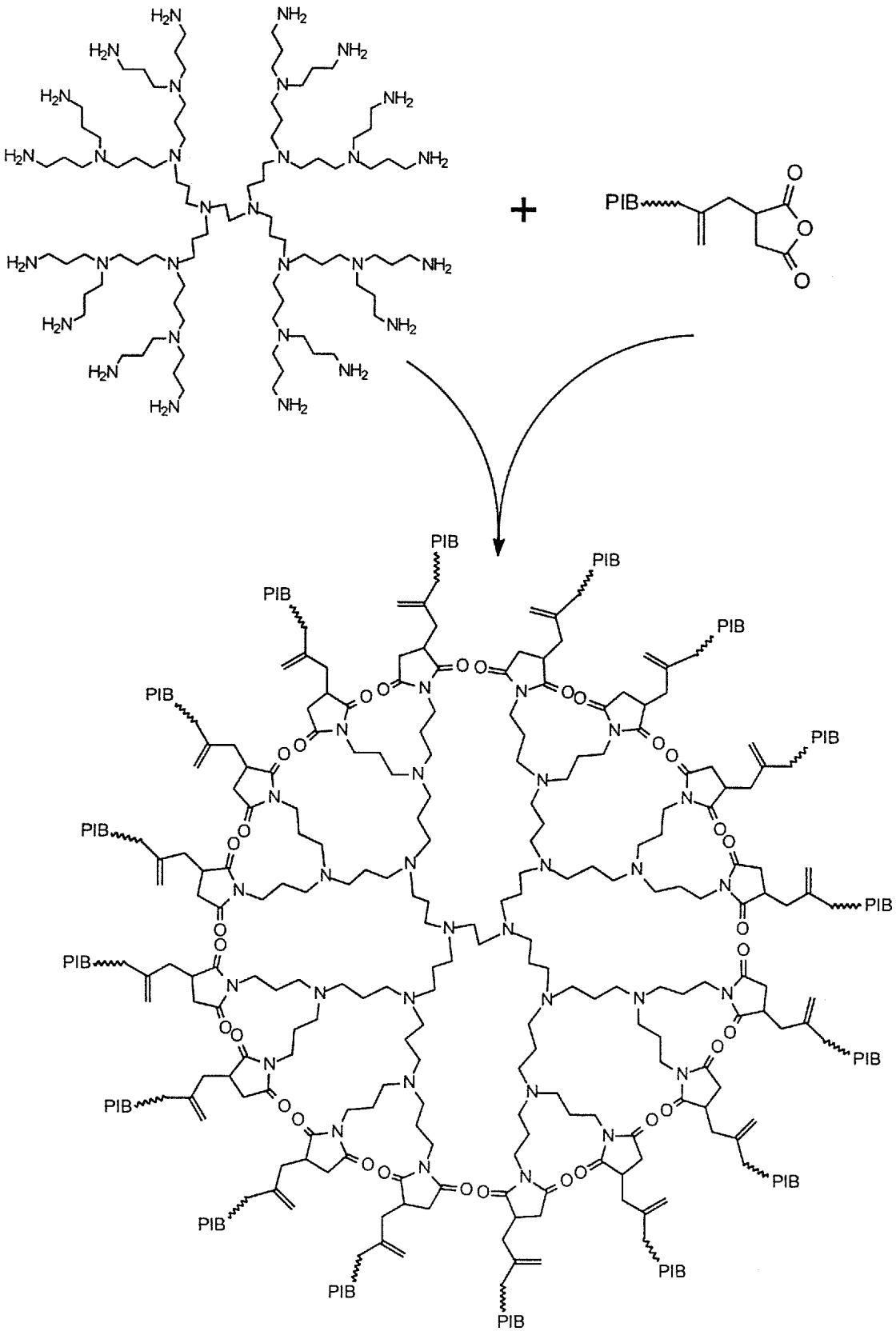
The crude product from the reaction was a mixture of the desired modified dendrimer, free PIB chains (from PIB-SA) and a small amount of PIB-SA (since a small excess of PIB-SA was used in the reaction). Removal of the low MW PIB and PIB-SA from the high MW dendrimer-PIB copolymers was not as easy as expected because the three species have similar solubilities in most common organic solvents. Eventually, it was found that the dendrimer-PIB1 copolymers could be purified by slow addition of acetone to their hexane solution. The copolymers separate from the solution as a yellow viscous liquid, while the free PIB chains remain in solution and can therefore be removed. The efficiency of the purification procedure was examined by ^{1}H-NMR and HPLC. Before purification, the proton spectra of crude copolymers shows a peak at 5.15 ppm due to the protons of "endo" double bonds from PIB-U and a peak at 4.64 ppm due to the protons of "exo" double bonds from PIB-U. After purification, these peaks disappear completely (see Figure 3c), indicating that all free PIB chains have been removed from the copolymers. However, this method could not be applied to the purification of copolymers of dendrimer-PIB2 because the high MW PIB2 also precipitated. As a result, these copolymers had to be purified by preparative HPLC for analytical purposes. It is clear however that in practical applications the crude product mixture would likely be entirely satisfactory for most purposes.

Conventional GPC analysis using THF as eluent proved to be suitable only for the generation one modified dendrimers, higher generations of the PIB modified dendrimers tend to stick to the GPC columns and could not be eluted. Attempt to use more polar solvents as eluent failed because the dendrimer-PIB copolymers are not soluble in polar solvents, such as DMF, NMP and DMSO.

3. HPLC analysis and purification of dendrimer-PIB2 copolymers

As a result of the difficulty in purification and characterization of the dendrimer-PIB copolymers, a new HPLC method was developed both for their analytical characterization and for the preparative scale separation of the PIB modified dendrimers. A column packed with porous monodisperse poly(2,3-dihydroxypropyl methacrylate-co-ethylene dimethacrylate) beads developed in our laboratories (14) was used for normal

Scheme 2



phase chromatographic analysis and also for the purification of dendrimer-PIB copolymers. We have shown earlier that these novel beads with diol functionalities represent a very sensitive medium that can easily separate molecules or macromolecules that only differ slightly in polarity (14). In this work, a gradient of acetone in hexane was used as the mobile phase and the presence of polymer in the effluent was monitored using an evaporative light-scattering detector. Figure 4a, b and c show the HPLC chromatograms of the crude star copolymers of G-1, G-3 and G-4 and PIB before purification. The free PIB chains appear as a sharp and large unretained peak with the retention time of 0.5 min. Also, the sharp peak of PIB-SA with retention time of 2.4 min was detected in reaction products containing G-3 and G-4 copolymers. The G-1 copolymer elutes as a single sharp peak at about 3.3 min, while the G-3 and G-4 elute as broad multiple peaks, which may be assigned to copolymers with different PIB chains attached to the dendrimers. Quantitative analysis shows that all these three crude copolymers contain about 61% of desired dendrimer-PIB star copolymer, 36% of free PIB-U and 2-3% of PIB-SA (G-3 and G-4). Since our analytical HPLC system provides very good separation of the crude copolymers from unreacted polymer, we tried to use the same separation medium packed in a larger column for the preparative separation of these samples on a scale of 0.5 gram per injection. The weight of the polymer in all of the collected fractions corresponded typically to more than 90 wt.% of the polymer loaded into the column. The purity of the copolymers after preparative HPLC separation was examined by analytical HPLC. As seen in Figure 4a', free PIB chains were completely removed from the G-1 copolymer, suggesting that the HPLC purification was very efficient. Unreacted PIB and PIB-SA can still be observed for the G-3 and G-4 copolymers (Figure 4b' and 4c'). However, the peaks for PIB and PIB-SA are much reduced when compared to those of the crude materials, and quantitative analysis shows

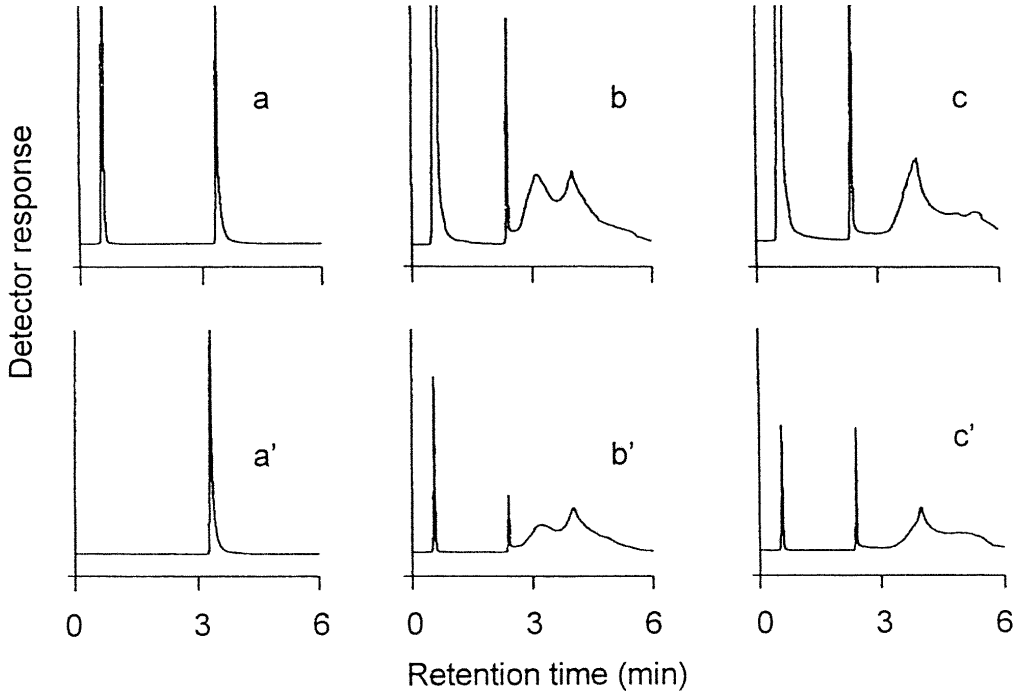


Fig 4. HPLC chromatograms of dendrimer-PIB2 copolymers before HPLC purification: (a) G-1, (b) G-3, (c) G-4 and after HPLC purification: (a') G-1, (b') G-3, (c') G-4.

that they represent only about 0.2% (for PIB) and 1.0% (for PIB-SA) of the samples by weight. This lack of complete separation may be due to the increased entanglement of free PIB chains with the copolymers as the generation of dendrimers increases.

Acknowledgment
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